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Citation: Lewis, Frank, Harwood, Laurence, Hudson, Michael, Drew, Michael, Sypula, Michal, Modolo, Giuseppe, Whittaker, Daniel, Sharrad, Clint, Videva, Vladimira, Hubscher-Bruder, Veronique and Arnaud-Neu, Françoise (2012) Complexation of lanthanides, actinides and transition metal cations with a 6-(1,2,4-triazin-3-yl)-2,2':6',2''-terpyridine ligand: implications for actinide(III) /lanthanide(III) partitioning. Dalton Transactions, 41. pp. 9209-9219. ISSN 0300-9246

Published by: Royal Society of Chemistry

URL: <http://dx.doi.org/10.1039/C2DT30522D> <<http://dx.doi.org/10.1039/C2DT30522D>>

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ARTICLE

Complexation of lanthanides, actinides and transition metal cations with a 6-(1,2,4-triazin-3-yl)-2,2':6',2''-terpyridine ligand: implications for actinide(III)/lanthanide(III) partitioning

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The quadridentate *N*-heterocyclic ligand 6-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2':6',2''-terpyridine (CyMe₄-hemi-BTBP) has been synthesized and its interactions with Am(III), U(VI), Ln(III) and some transition metal cations have been evaluated by X-ray crystallographic analysis, Am(III)/Eu(III) solvent extraction experiments, UV absorption spectrophotometry, NMR studies and ESI-MS. Structures of the 1:1 complexes with Eu(III), Ce(III) and the linear uranyl (UO₂²⁺) ion were obtained by X-ray crystallographic analysis, and showed similar coordination behavior to related BTBP complexes. In methanol, the stability constants of the Ln(III) complexes are slightly lower than those of the analogous quadridentate bis-triazine BTBP ligands, while the stability constant for the Yb(III) complex is higher. ¹H NMR titrations and ESI-MS with lanthanide nitrates showed that the ligand forms only 1:1 complexes with Eu(III), Ce(III) and Yb(III), while both 1:1 and 1:2 complexes were formed with La(III) and Y(III) in acetonitrile. A mixture of isomeric chiral 2:2 helical complexes was formed with Cu(I), with a slight preference (1.4:1) for a single directional isomer. In contrast, a 1:1 complex was observed with the larger Ag(I) ion. The ligand was unable to extract Am(III) or Eu(III) from nitric acid solutions into 1-octanol, except in the presence of a synergist at low acidity. The results show that the presence of two outer 1,2,4-triazine rings is required for the efficient extraction and separation of An(III) from Ln(III) by quadridentate *N*-donor ligands.

Introduction

A major goal in the future treatment of used nuclear fuel is the reduction in the long-term radiotoxicity of the waste by the removal of the long-lived minor actinides. In the partitioning and transmutation (P&T) strategy,¹ it is intended that, following their separation from the trivalent lanthanides, the trivalent minor actinides Am(III) and Cm(III) will be converted into shorter-lived or stable elements by neutron bombardment. Since many lanthanides have high neutron capture cross sections, efficient transmutation of the actinides is only possible once they have first been separated (partitioned) from the lanthanides.²

Although the chemical properties of An(III) and Ln(III) are similar,³ it has been shown that ligands containing soft *N*- and *S*-donor atoms are capable of separating the two groups of elements.⁴ The selectivity of these reagents for An(III) over Ln(III) is believed to arise from a more covalent interaction between the donor atoms of the ligands and the 5f orbitals of An(III).⁵ Within the soft *N*-donor ligands, bis-(1,2,4-triazine) ligands show the highest selectivities and optimum extraction performances to date. The terdentate 2,6-bis(1,2,4-triazin-3-yl)pyridine (BTP)⁶ and the quadridentate 6,6'-bis(1,2,4-triazin-3-

yl)-2,2'-bipyridine (BTBP)⁷ ligands have been the focus of intensive research. The annulated ligand CyMe₄-BTBP **1**⁸ (Figure 1) is currently the most suitable for An(III)/Ln(III) separations, as recently demonstrated under process conditions.⁹ It has also been shown that the extraction properties of **1** can be markedly improved by pre-organization of the ligand using a 1,10-phenanthroline moiety.¹⁰

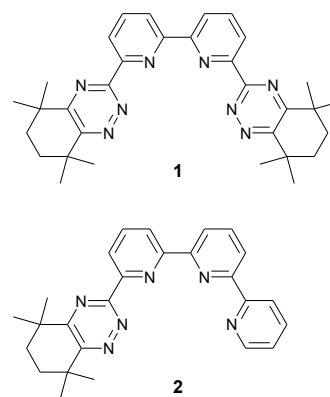


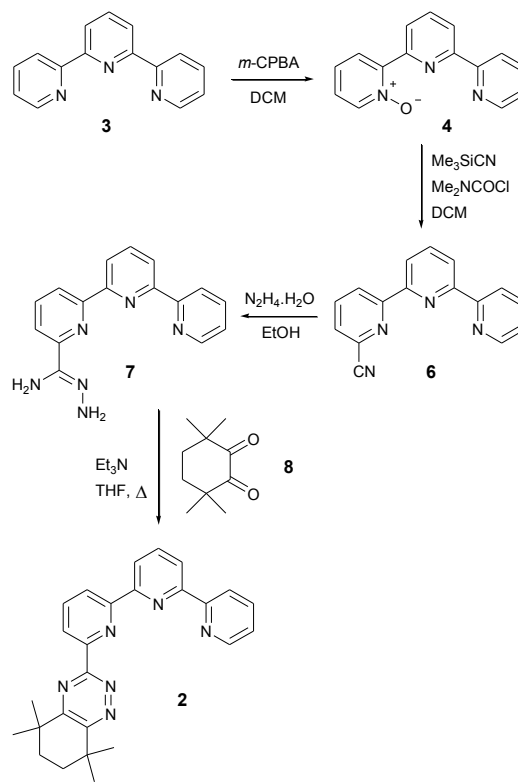
Figure 1. Structures of CyMe₄-BTBP **1** and CyMe₄-hemi-BTBP **2**.

Despite intensive research,¹¹ a fundamental understanding of the origins of the high selectivities and excellent extraction properties shown by bis-(1,2,4-triazine) ligands is still limited, with the result that further improvements in ligand design continue to be made largely on a trial and error basis using chemical intuition. Previous studies on tridentate heterocyclic *N*-donor ligands have shown that the 6-(1,2,4-triazin-3-yl)-2,2'-bipyridine ligands (hemi-BTPs)¹² have properties intermediate between those of the BTPs and the 2,2':6',2''-terpyridine ligands (TERPY).¹³ However, the hemi-BTPs more closely resemble the TERPY ligands in their extraction behaviour (ie: only 1:1 complexes are formed in contrast to the more hydrophobic 1:3 complexes formed by the BTPs, extraction only occurs at low acidity and a synergist is required for extraction to take place). With the aim of furthering our understanding of the quadridentate BTBP ligands, we report herein the results of our investigations on a closely related quadridentate 6-(1,2,4-triazin-3-yl)-2,2':6',2''-terpyridine (hemi-BTBP) ligand CyMe₄-hemi-BTBP **2** (Figure 1), in which one of the triazine rings of **1** has been replaced by a pyridine ring.

Results and Discussion

Synthesis and X-ray Crystallography

The new ligand CyMe₄-hemi-BTBP **2** was synthesized in four steps as shown in Scheme 1. Oxidation of 2,2':6',2''-terpyridine **3** with 3-chloroperoxybenzoic acid (*m*-CPBA)¹⁴ generated a mixture of mono-*N*-oxide **4**,¹⁵ bis-*N*-oxide **5**¹⁶ and unreacted **3** from which **4** was obtained pure in 52% yield after separation by column chromatography. A modified Reissert-Henze reaction¹⁷ of **4** with trimethylsilyl cyanide and *N,N*-dimethylcarbamyl chloride afforded the nitrile **6**¹⁸ in high yield (**CAUTION**: trimethylsilyl cyanide is a volatile hydrogen cyanide equivalent). The reaction of **6** with hydrazine hydrate gave the carbohydrazonamide **7**¹⁹ which, on treatment with 3,3,6,6-tetramethylcyclohexane-1,2-dione **8**^{20,21} in THF/Et₃N at reflux furnished the ligand **2** in 93% yield (see Supporting Information for the synthesis of compounds 4–7).



Scheme 1. Synthesis of CyMe₄-hemi-BTBP **2**.

The X-ray crystal structure of **2** is shown in Figure 2 together with the atomic numbering scheme. The four aromatic rings are in a mutually *trans*- arrangement with respect to the pyridine nitrogen atoms. Thus the N(11)–C–C–N(21), N(21)–C–C–N(31) and N(31)–C–C–N(41) torsion angles are –157.7(2), –172.7(2) and –19.1(2)°, respectively. This *trans*, *trans*- arrangement of adjacent pyridine rings has been shown previously by quantum mechanics calculations¹² to be the most energetically favourable arrangement, primarily because there are no close H–H contacts between adjacent rings. Clearly, this conformation needs to change before the ligand can bind to a metal cation through its four nitrogen atoms. In previous work on multidentate *N*-donor ligands containing 1,2,4 triazine rings, it is always found that binding occurs through the nitrogen in position 2 of the triazine ring.²² The packing of **2** in the crystal is shown in Figure 17 in the Supporting Information. The molecules pack in pairs across a centre of symmetry, enabling π – π stacking between their central pyridine rings. The distance between these central pyridine rings (containing N(31)) is 3.32 Å.

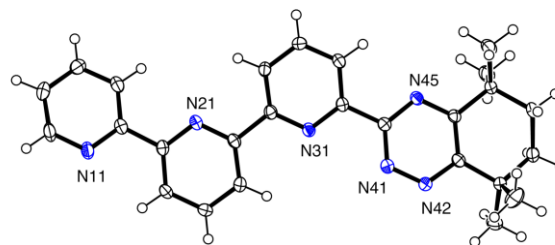


Figure 2. X-ray crystal structure of CyMe₄-hemi-BTBP **2**.

We also synthesized the 1:1 complexes of **2** with the lanthanide nitrates $\text{Eu}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ by admixture of dichloromethane solutions of **2** with a solution of the lanthanide nitrate salt in CH_3CN , followed by evaporation of the solvent.

Coordination of the paramagnetic lanthanides to the ligand **2** induced marked shifts in the ^1H NMR spectra of the complexes, particularly in the case of $\text{Eu}(\text{III})$. In the $\text{Eu}(\text{III})$ complex, three of the aromatic protons of **2** are shifted upfield to 3.44, 4.02 and 4.91 ppm while the methyl resonances are shifted downfield from 1.48 and 1.53 ppm to 2.68 and 2.91 ppm. The methylene protons appear as a multiplet at 3.04–3.14 ppm. Slow evaporation of solutions of the Eu and Ce complexes of **2** in $\text{MeOH}/\text{dichloromethane}/\text{toluene}$ afforded crystals of the complexes suitable for X-ray analysis. The X-ray crystal structure of the Eu complex of **2** is shown in Figure 3.

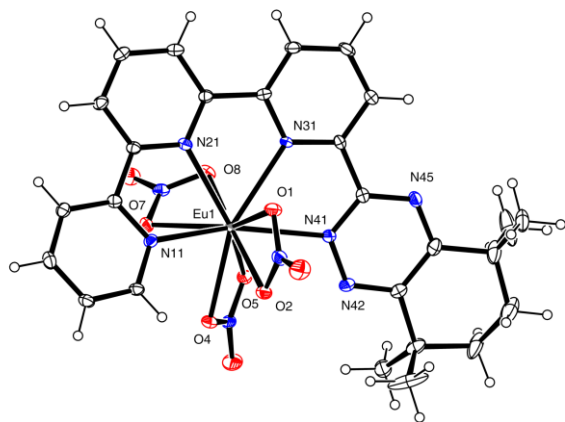


Figure 3. X-ray crystal structure of $[\text{Eu}(\mathbf{2})(\text{NO}_3)_3] \cdot 2\text{MeCN}$. Ellipsoids are shown at 30 % probability. Solvent molecules are omitted for clarity.

As is evident, the ligand coordinates in an approximately distorted planar tetradentate fashion to the Eu metal centre which is 10-coordinate. The remainder of the metal's inner coordination sphere is made up of three bidentate nitrate ions. The $\text{Eu}-\text{N}$ bond distances range from 2.523(4) to 2.564(4) Å. A similar structure was also obtained with $\text{Ce}(\text{NO}_3)_3$ (Figure 4). The $\text{Ce}-\text{N}$ bond distances in this structure range from 2.605(8) to 2.621(8) Å. The difference in $\text{M}-\text{N}$ bond lengths reflect the smaller size of the Eu ion compared to the Ce ion. The coordination mode of ligand **2** in these complexes is quite similar to that observed in the 1:1 complexes formed by the analogous BTBP ligands with trivalent lanthanide nitrates,²³ while the bond lengths are comparable. Some notable differences are that, in the present case, ligand **2** is significantly more distorted from planarity than the BTBP ligands in their 1:1 lanthanide complexes, and the orientation of the three nitrate ligands relative to the equatorial plane of the ligand is also different. The $\text{N}(11)-\text{C}-\text{C}-\text{N}(21)$, $\text{N}(21)-\text{C}-\text{C}-\text{N}(31)$ and $\text{N}(31)-\text{C}-\text{C}-\text{N}(41)$ torsion angles for the Eu and Ce complexes are 2.0(6), 14.3(6), 2.1(6)°, and -2.0(7), 19.5(4) and -0.5(3)°, respectively which may well show that the $\text{Eu}(\text{III})$ ion is a better fit into the coordination cavity of **2** than the larger $\text{Ce}(\text{III})$ ion. The metal is also oriented well away from the plane of the four ligating nitrogens in the Eu and Ce structures (r.m.s. deviations of Eu and Ce from the plane of the four nitrogen atoms are 0.52(1) and 0.48(1) Å, respectively).

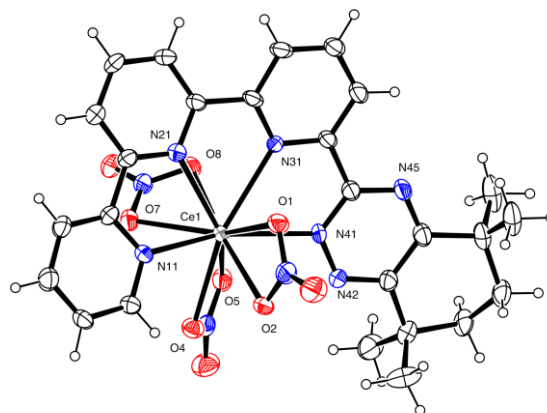


Figure 4. X-ray crystal structure of $[\text{Ce}(\mathbf{2})(\text{NO}_3)_3] \cdot \text{C}_7\text{H}_8$. Ellipsoids are shown at 30 % probability. Solvent molecules are omitted for clarity.

Addition of a dichloromethane solution of **2** to a solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in methanol/acetonitrile afforded a sample of the uranyl complex $[\text{UO}_2(\mathbf{2})\text{MeOH}][\text{UO}_2(\text{NO}_3)_4]$ from which crystals suitable for X-ray analysis were obtained following slow evaporation. The X-ray structure of this complex is presented in Figure 5. The uranyl ion is coordinated in the classic pentagonal bipyramidal configuration which is well known for actinyl ions.²⁴ In contrast to the Eu and Ce structures, the ligand **2** is almost planar and coordinates to the metal perpendicular to the linear UO_2^{2+} axis. The four $\text{U}-\text{N}$ bond lengths range from 2.517(6) to 2.580(5) Å while the $\text{U}=\text{O}$ bond lengths are $\text{U}(2)-\text{O}(9) = 1.767(5)$ and $\text{U}(2)-\text{O}(10) = 1.766(5)$ Å, which are typical of uranyl complexes. The UO_2^{2+} cation is almost linear ($\text{O}(9)-\text{U}(2)-\text{O}(10)$ bond angle = 175.6(2)°). The remaining coordination site in the equatorial plane is occupied by a MeOH molecule. The structure is identical to analogous uranyl structures derived from $\text{CyMe}_4\text{-BTBP}$ **1** reported previously, and there are no significant differences in the $\text{U}-\text{N}$ bond lengths.²⁵

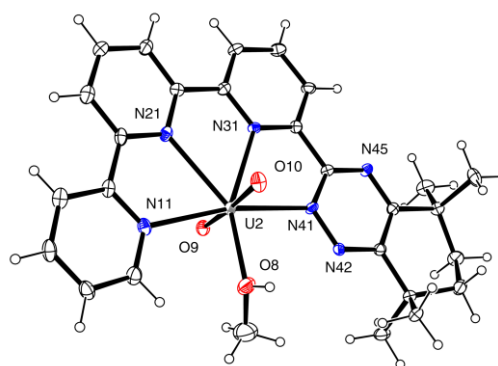


Figure 5. X-ray crystal structure of $[\text{UO}_2(\mathbf{2})\text{MeOH}][\text{UO}_2(\text{NO}_3)_4]$. Ellipsoids are shown at 30 % probability. The counterion is not shown.

Similarly, $\text{Cu}(\text{I})$ and $\text{Ag}(\text{I})$ complexes of **2** were prepared by admixture of **2** with $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ and $[\text{Ag}(\text{MeCN})_4]\text{BF}_4$. Detailed NMR and ESI-MS studies (*vide supra*) revealed that the stoichiometries of these complexes were 2:2 and 1:1, respectively. Unfortunately, despite repeated attempts at crystal growing, efforts to characterize these complexes by X-ray

crystallographic analysis were unsuccessful.

Solvent Extraction Studies

Ligand **2** was then studied for its ability to extract and separate Am(III) and Eu(III) from nitric acid solutions into *n*-octanol, one of the most common diluents used for An/Ln separations. The distribution ratios and separation factors for the extraction of Am(III) and Eu(III) from nitric acid solutions by **2** dissolved in *n*-octanol (0.01 M) are shown in Table 1. Low distribution ratios ($D < 0.01$) were obtained for both Am(III) and Eu(III) at all nitric acid concentrations from 0.01–4 M, and essentially no significant extraction of either metal ion takes place. Furthermore, the ligand **2** shows no significant selectivity for Am(III) over Eu(III). These results are in marked contrast to those obtained for related quadridentate bis-triazine ligands such as CyMe₄-BTBP **1** which can extract ($D_{\text{Am}} > 1$) and separate Am(III) from Eu(III) with high selectivities ($\text{SF}_{\text{Am/Eu}} \sim 100$) under similar conditions.⁸

Table 1. Extraction of Am(III) and Eu(III) by CyMe₄-hemi-BTBP **2** into 1-octanol (0.01 M) as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO ₃]	D_{Am}	D_{Eu}	$\text{SF}_{\text{Am/Eu}}$
0.01	0.0003 ± 0.0001	0.0004 ± 0.0001	0.7 ± 0.1
0.1	0.0005 ± 0.0001	0.0003 ± 0.0001	1.6 ± 0.3
1.0	0.0007 ± 0.0001	0.0003 ± 0.0001	2.2 ± 0.4
2.0	0.0010 ± 0.0002	0.0013 ± 0.0003	0.8 ± 0.2
3.0	0.0015 ± 0.0003	0.0019 ± 0.0004	0.8 ± 0.2
4.0	0.0021 ± 0.0004	0.0021 ± 0.0004	1.0 ± 0.2

It has been shown in previous studies on polydentate heterocyclic *N*-donor ligands that the extractions of An(III) and Ln(III) from nitric acid can be improved considerably by the inclusion of a lipophilic anion source (eg: 2-bromodecanoic acid) as a synergist in the organic phase.¹³ However, this effect only takes place at low acidity because dissociation of the synergist is suppressed at low pH. Thus the extraction experiments with **2** were repeated in the presence of 2-bromohexanoic acid (see Table 1 and Figure 18 in the Supporting Information). As expected, the extraction of Am(III) improves at low [HNO₃] ($D_{\text{Am}} = 1.3$ at 0.001 M HNO₃) but the distribution ratios decrease again at higher acidities. The above results demonstrate that replacement of one of the 1,2,4-triazine rings in the BTBP ligands with a pyridine ring leads to a marked decrease in extraction performance and selectivity, and show that two 1,2,4-triazine rings are important for optimum results. A similar effect has previously been observed when one of the 1,2,4-triazine rings of the tridentate BTP ligands was replaced with a pyridine ring.¹²

Metal Ion Complexation Studies

Using previously published methods,²⁶ the complexing properties of **2** with three lanthanide ions (La(III), Eu(III) and Yb(III)) and two transition metal ions (Cu(II) and Ni(II)) were studied in methanol and nitrate media using absorption-spectrophotometry. For comparison, the same measurements were also performed with the related ligand CyMe₄-BTTP **9** (Figure 6).²⁷

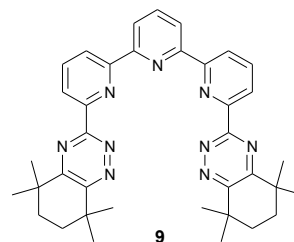


Figure 6. Structure of the ligand CyMe₄-BTTP **9**.

Initially, the stability with time of the ligand solutions was checked spectrophotometrically, as well as the time-dependence of the absorbances of mixtures of the ligands in the presence of *ca.* one equivalent of the metal. While for La(III) and Cu(II) the equilibria were always reached within the time scale of the measurements, it was necessary to wait longer to reach the equilibrium for Eu(III) (10 min with CyMe₄-BTTP **9**) and particularly for Yb(III) (10 min with CyMe₄-hemi-BTBP **2** and 15 min with CyMe₄-BTTP **9**) and Ni(II) (15 min with CyMe₄-hemi-BTBP **2**). For every system studied, complexation led to significant spectroscopic changes giving rise in most cases to one or more isosbestic points. The spectrophotometric titration of CyMe₄-hemi-BTBP **2** with Yb(III) is presented in Figure 7 as an example.

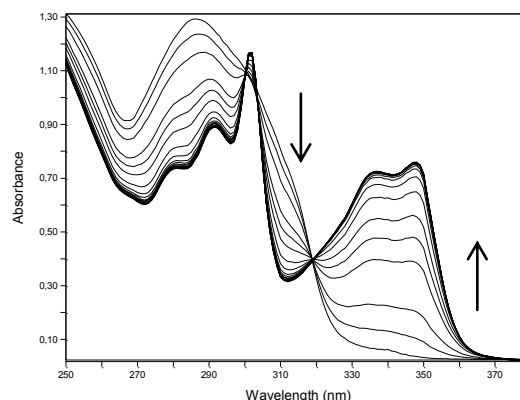


Figure 7. Spectrophotometric titration of CyMe₄-hemi-BTBP **2** ($C_{\text{L}} = 5.16 \times 10^{-5}$ M) with Yb(NO₃)₃ in methanol ($0 \leq C_{\text{M}}/C_{\text{L}} \leq 1.94$) ($T = 25$ °C, $I = 10^{-2}$ M Et₄NNO₃).

As regards lanthanide complexation, the best fit of the experimental data is obtained assuming the formation of 1:1 complexes of CyMe₄-hemi-BTBP **2** and of CyMe₄-BTTP **9** with the two cations Eu(III) and Yb(III). With both ligands and Yb(III), the fit is improved considering an additional 1:2 complex. The 1:1 stoichiometries of the lanthanide(III) nitrate complexes with ligand **9** are consistent with those found in the solid state and in liquid-liquid extraction of Eu(III) from nitric acid into octanol.²⁷ For La(III), the best interpretation points to the formation of an exclusive 1:1 complex with **2** and a 1:2 complex with **9**. The corresponding stability constants ($\log \beta$) are given in Table 2. The results show that, in the case of **2**, the stability constants of the 1:1 complexes with La(III) and Eu(III) are slightly lower than those found for the analogous CyMe₄-BTBP **1** (determined previously),²⁶ while the corresponding complex with Yb(III) is more stable. The stability constants of the complexes of the same stoichiometry with CyMe₄-BTTP **9**

and the related CyMe₄-BTBP **1** are of the same order of magnitude (except for Eu(III)), suggesting similar coordination. Regarding Ni(II), the best model corresponds to the formation of complexes of 1:2 and 1:3 stoichiometries for each ligand. No satisfactory model has been found so far for the complexation of Cu(II) by either ligand.

Table 2. Stability constants (log β) of some lanthanide(III) and nickel(II) complexes with ligands **1**, **2** and **9** in methanol (T = 25 °C, I = 10⁻² M Et₄NNO₃) determined by UV-vis spectrometry.

Ligand	Complex	La(III)	Eu(III)	Yb(III)	Ni(II) ^b
1 ^a	1:1	4.4	6.5	5.9	–
	1:2	8.8	11.9	–	–
2	1:1	4.29 ± 0.08	5.6 ± 0.4	7.3 ± 0.2	–
	1:2	–	–	12.4 ± 0.2	9.95 ± 0.08
	1:3	–	–	–	15.4 ± 0.1
9	1:1	–	5.5 ± 0.2	5.6 ± 0.1	–
	1:2	8.2 ± 0.3	–	9.9 ± 0.5	12.1 ± 0.2
	1:3	–	–	–	16.9 ± 0.2

^a Determined previously.²⁶ ^b One experiment.

NMR Titrations

The coordination chemistry and speciation of CyMe₄-hemi-BTBP **2** with selected trivalent lanthanide nitrates and transition metals was then studied by ¹H NMR titration.²⁸ This technique is a useful tool for the determination of the solution behaviour of ligands with metal cations.²⁹ The formation of metal complexes of **2** was followed by recording ¹H NMR spectra of a solution of **2** (0.01 M) in CD₃CN to which solutions of the metal salts (0.01 M in CD₃CN) were progressively added. In the titration of **2** with La(NO₃)₃, both 1:1 and 1:2 complexes were observed. The 1:2 species is the major solution species present at low metal:ligand ratios. However, at higher metal:ligand ratios the 1:1 complex becomes the dominant solution species and this is the only species present after 1.3 equivalents of La(NO₃)₃ have been added (see Figures 19 and 20 in the Supporting Information). Clearly, both 1:1 and 1:2 complexes are in equilibrium, and their relative ratio depends on the metal:ligand ratio. The species distribution curve, presented in Figure 8, was calculated from the normalized relative ratios of each of the species present (obtained by integration of a given resonance for each species).

The stoichiometry of the 1:1 species formed at the end of the titration was confirmed by ESI-MS (see Figure 21 in the Supporting Information). A mass peak corresponding to [La(2)(NO₃)₂]⁺ was observed at *m/z* = 685.1039. The isotope distribution pattern of this peak was in agreement with that expected for [La(2)(NO₃)₂]⁺. In a related ESI-MS study on BTBP ligands, only the 1:2 complexes were formed with lanthanides under extraction conditions.³⁰

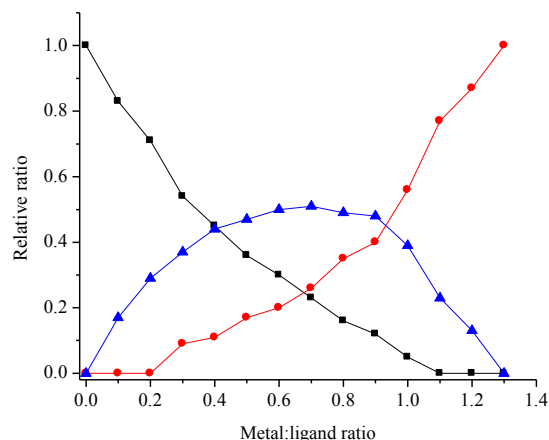


Figure 8. ¹H NMR titration of CyMe₄-hemi-BTBP **2** with La(NO₃)₃ in CD₃CN (■ = free ligand, ● = 1:1 complex, ▲ = 1:2 complex).

In the case of Eu(NO₃)₃, only a 1:1 species was formed during the course of the titration with **2**, and the resonances of the free ligand completely disappear after 1.1 equivalents of Eu(III) have been added. The paramagnetic Eu(III) ion induced pronounced shifts in some of the aromatic protons of **2**, although well resolved spectra were still obtained (see Figures 22 and 23 in the Supporting Information).³¹ This is often the case with Eu(III) complexes because the Eu(III) cation usually causes minimal broadening of NMR peaks. The species distribution curve (see Figure 24 in the Supporting Information) displayed a slightly asymptotic behaviour at the beginning of the titration, suggesting that the complexation reaction was incomplete. A straight line would be expected if all of the added Eu(III) was complexed by **2**. A slow complexation reaction was ruled out on the basis that no spectroscopic changes were observed as a function of time. The ¹H NMR spectrum of the 1:1 complex [Eu(2)(NO₃)₃] is shown in Figure 9. In the ESI-MS spectrum of the final solution species, a mass peak corresponding to [Eu(2)(NO₃)₂]⁺ was observed (see Figure 25 in the Supporting Information). The stoichiometries of the La(III) and Eu(III) complexes deduced from ¹H NMR and ESI-MS are in agreement with those determined spectrophotometrically in methanol.

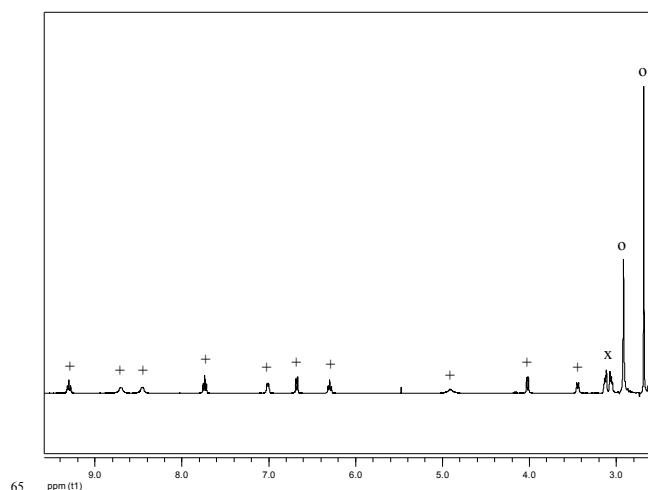


Figure 9. ^1H NMR spectrum of the 1:1 complex $[\text{Eu}(\mathbf{2})(\text{NO}_3)_3]$ in CD_3CN (Assignments: o = methyl groups, x = methylene protons, + = aromatic protons).

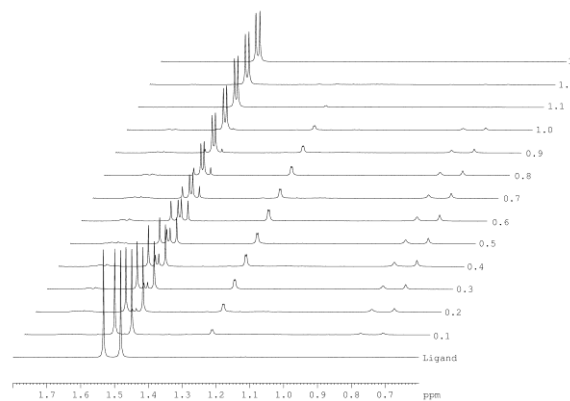


Figure 10. Aliphatic region of the stack plot for the titration of CyMe_4 -hemi-BTBP **2** with $\text{Y}(\text{NO}_3)_3$. First (bottom) spectrum = free ligand. Each subsequent spectrum corresponds to the addition of 0.1 eq. of $\text{Y}(\text{NO}_3)_3$.

We then extended our NMR study to the complexation of **2** with $\text{Cu}(\text{I})$ and $\text{Ag}(\text{I})$. Extensive studies on oligopyridine coordination chemistry³³ by Constable and others have shown that the quaterpyridine ligands typically form planar mononuclear 1:1 complexes with metals that favour square planar or octahedral coordination geometries (eg: $\text{Ni}(\text{II})$, $\text{Pd}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$).^{34,35} On the other hand, metals that favour tetrahedral coordination geometries (eg: $\text{Cu}(\text{I})$, $\text{Ag}(\text{I})$) usually form dinuclear double-helical 2:2 complexes,³⁶ although some rare exceptions have been noted.³⁷ Non-symmetrical quaterpyridine ligands are of particular interest as they are capable of forming directional isomers (head-to-head or head-to-tail isomers) when they form dinuclear double-helicates.³⁸ CyMe_4 -hemi-BTBP **2** can be considered as a non-symmetrical quaterpyridine mimic, and we thus studied its complexation with CuBF_4 and AgBF_4 by NMR spectroscopy.

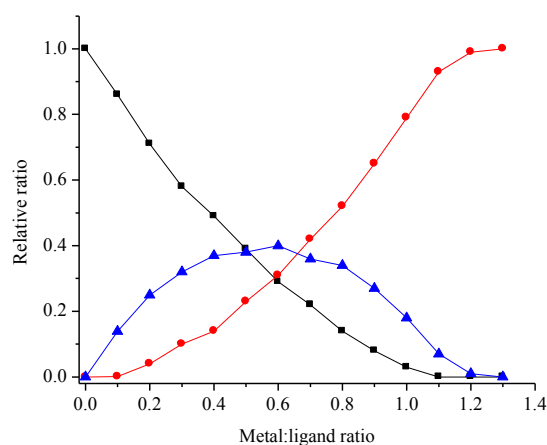


Figure 11. ^1H NMR titration of CyMe_4 -hemi-BTBP **2** with $\text{Y}(\text{NO}_3)_3$ in CD_3CN (■ = free ligand, ● = 1:1 complex, ▲ = 1:2 complex).

During the titration of **2** with CuBF_4 , seven new resonances were observed for the methyl groups while the methylene protons appeared as a complex multiplet at 1.81–1.93 ppm (see Figures 35–37 in the Supporting Information). Four methyl group resonances would be expected for a single isomer of a 2:2 helical complex (such a complex would be chiral with a screw axis, and the methyl groups would be diastereotopic) while only two would

be expected for an achiral 1:1 complex. Two directional isomers of a dinuclear double-helical 2:2 complex are thus apparently formed (two of the resonances are overlapping).

Another possibility is that the ligand forms a 1:2 complex with each ligand being bidentate. Such a complex would also be chiral and four resonances would then be expected for the methyl groups. However, no directional isomerism is possible in such a structure and the maximum number of methyl resonances observed would only be four. The aliphatic region of the ^1H NMR spectrum of the final species formed after 1.2 equivalents of Cu(I) have been added is shown in Figure 12. The 2:2 stoichiometry of the complex was also verified by ESI-MS (see Figure 39 in the Supporting Information). The isotope distribution pattern of the mass peak ($m/z = 485.1490$) was consistent with a species containing two Cu(I) ions (7 mass peaks separated by 0.5 mass units).³⁹

The relative ratios of the methyl resonances are not equal and the ratio of directional isomers was calculated as 1.4:1 based on the relative integrations of the two sets of methyl resonances. Further evidence for the formation of two isomers of a 2:2 complex is found in the ^{13}C NMR spectrum of the final complex, which shows a doubling of all the expected resonances (ie: 8 methyl groups, 4 methylene carbons, 20 aromatic carbons). The calculated species distribution curve is shown in Figure 38 in the Supporting Information. The linear shape of the curve is indicative of a complexation reaction that goes to completion.

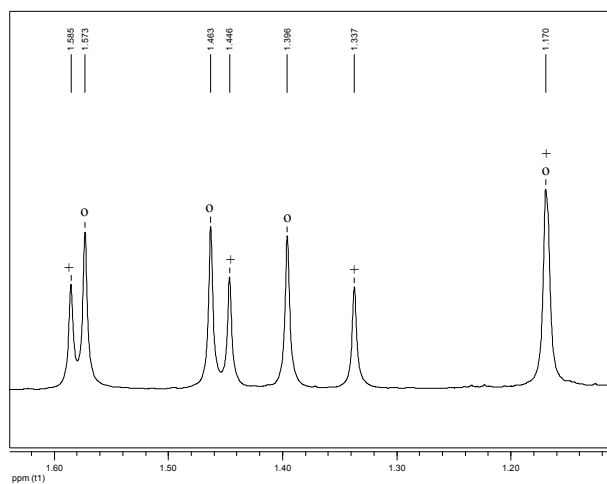


Figure 12. Aliphatic region of the ^1H NMR spectrum of $[\text{Cu}_2(\mathbf{2})_2](\text{BF}_4)_2$ in CD_3CN (Assignments: o = methyl groups of major isomer, + = methyl groups of minor isomer).

In contrast to the above results, the titration of **2** with AgBF_4 did not show separate resonances for the free ligand and the complexes. Instead, an averaged NMR spectrum of both species was observed throughout the titration (see Figures 40 and 41 in the Supporting Information). Only one set of resonances was observed (two methyl peaks, one methylene resonance, one set of aromatic peaks), with minor changes in chemical shift occurring in some cases until 1.1 equivalents of metal had been added, after which no further spectroscopic changes were observed. This suggests that a rapid exchange process is taking place faster than the NMR timescale can detect. The presence of only two resonances for the methyl groups indicates that an achiral 1:1 complex is formed. A helical structure can thus be ruled out. The

1:1 complex stoichiometry was verified by ESI-MS (see Figure 42 in the Supporting Information). The formation of a 1:1 complex in this case is likely due to a better size fit of the larger Ag(I) ion in the planar tetradentate coordination cavity of **2**. Although rare, examples of planar 1:1 complexes of Ag(I) with analogous quaterpyridine³⁷ and quinquepyridine⁴⁰ ligands have been reported.

Conclusions

We have synthesized the quadridentate *N*-donor ligand **2** related to the established BTBP ligands which are currently the benchmark ligands for An(III)/Ln(III) separations, in which one of the outer 1,2,4-triazine rings of the BTBP ligand has been replaced by a pyridine ring. The extraction selectivity for An(III) over Ln(III), and the extraction performance were found to be inferior to those of the BTBPs, possibly due to competing protonation of the ligand. Interestingly, the extraction performance of the ligand is comparable to that of $\text{CyMe}_4\text{-BTTP}$ **9** (Figure 6), which was capable of forming only 1:1 complexes in nitrate media.²⁷ Solid state structures of the 1:1 complexes of the ligand with Eu(III), Ce(III) and U(VI) were solved by X-ray crystallographic analysis. The lanthanide complexes showed a greater degree of ligand distortion compared to the 1:1 lanthanide BTBP complexes reported previously. Complexation results obtained in methanol show the formation of 1:1 complexes with all Ln(III) nitrates and of an additional 1:2 complex in the case of Yb(III). In acetonitrile, ligand **2** formed only 1:1 complexes with these cations, except in the cases of La(III) and Y(III) where equilibrium mixtures of 1:1 and 1:2 species were observed. This contrasts with the BTBP ligands which form predominantly 1:2 complexes in solution. The new ligand may be considered as an unsymmetrical quaterpyridine mimic, and the formation of two isomers of a chiral dinuclear double-helicate in solution was found with Cu(I). We suggest that the extraction ability of the quadridentate 1,2,4-triazine-based ligands is related to the relative ratios of 1:1 and 1:2 complexes formed. Thus the BTBPs form predominantly hydrophobic 1:2 complexes with An(III) and are able to extract An(III) from nitric acid medium, while in the present case, the hemi-BTBP ligand **2** forms only 1:1 complexes (except with the early lanthanides) that are less hydrophobic and thus more difficult to extract. The presence of at least two covalent interactions between 1,2,4-triazine rings and An(III) is obviously important for the formation of hydrophobic extractable 1:2 complexes by quadridentate *N*-donor ligands. The results highlight the importance of two outer 1,2,4-triazine rings as one important feature in extractant design, and help to further our understanding of the origins of the excellent extraction performances and An(III)/Ln(III) selectivities shown by bis-(1,2,4-triazine) *N*-donor ligands.

Experimental

Uncorrected melting points were obtained on a Stuart SMP10 instrument. IR spectra were recorded as Nujol[®] mulls on a Perkin Elmer RX1 FT-IR instrument. ^1H , ^{13}C - $\{^1\text{H}\}$ and ^{13}C NMR spectra were recorded using either a Bruker AMX400, an Avance DFX400 or an Avance DPX250 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane.

Assignments were verified with ^1H - ^1H and ^1H - ^{13}C COSY experiments as appropriate. Mass spectra were obtained under electrospray conditions on a Thermo Scientific LTQ Orbitrap XL instrument. Elemental microanalyses were performed by Medac Ltd., Chobham, Surrey (UK). All organic reagents were obtained from either Acros or Aldrich, while inorganic reagents were obtained from either BDH or Aldrich and used as received.

6-(5,5,8,8-Tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2':6',2''-terpyridine **2**

2,2':6',2''-Terpyridine-6-carbohydrazonomide **7**¹⁹ (1.51 g, 5.20 mmol) was suspended in THF (150 mL) and 3,3,6,6-tetramethylcyclohexane-1,2-dione **8** (1.05 g, 6.24 mmol, 1.2 eq) was added. Triethylamine (10 mL) was added and the suspension was heated under reflux for 24 hours. The solution was allowed to cool to room temperature and stirring was continued for a further 12 hours. The solvent was removed *in vacuo* and the residue was purified by chromatography, eluting first with DCM, then with 5 % MeOH in DCM to afford the title compound **2** as a yellow solid (2.05 g, 93%). Mp 182–184 °C (from MeOH/DCM). Found: C, 73.91; H, 6.20; N, 19.88%; $\text{C}_{26}\text{H}_{26}\text{N}_6$ requires C, 73.74; H, 6.24; N, 19.67%. $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 2926, 1580, 1560, 1507, 1458, 1375, 1263, 1141, 1075, 1042, 988, 920, 847, 811, 781, 737, 677, 629. $\delta_{\text{H}}(400.1 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.47 (6H, s, 2 × Me), 1.52 (6H, s, 2 × Me), 1.88 (4H, s, 2 × CH_2), 7.33 (1H, ddd, J 7.6, 4.8 and 1.1, 4''-H), 7.86 (1H, td, J 7.6 and 1.8, 5''-H), 8.00 (1H, t, J 7.8, 4'-H), 8.05 (1H, t, J 7.8, 4-H), 8.47 (1H, dd, J 7.8 and 1.0, 5'-H), 8.54 (1H, dd, J 7.7 and 1.0, 3-H), 8.65 (1H, dt, J 7.8 and 1.1, 6''-H), 8.71 (1H, ddd, J 4.8, 1.8 and 1.1, 3''-H), 8.80 (1H, dd, J 7.8 and 1.0, 5-H), 8.82 (1H, dd, J 7.8 and 1.0, 3'-H). $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 29.2 (2 × Me), 29.7 (2 × Me), 33.2 (CH_2), 33.7 (CH_2), 36.4 (quat), 37.2 (quat), 121.1 (C-6''), 121.2 (C-5'), 121.6 (C-3'), 122.2 (C-5), 123.6 (C-3), 123.7 (C-4''), 136.8 (C-5''), 137.7 (C-4), 137.9 (C-4'), 149.1 (C-3''), 152.9 (quat), 155.0 (quat), 155.1 (quat), 156.2 (quat), 156.3 (quat), 160.9 (quat), 163.0 (quat), 164.4 (quat). m/z (CI) 423.2298 ($[\text{M} + \text{H}]^+$); $\text{C}_{26}\text{H}_{27}\text{N}_6$ requires 423.2297.

Eu(NO_3)₃ Complex of CyMe₄-hemi-BTBP **2**

The ligand **2** (0.1065 g, 0.2522 mmol) was dissolved in DCM (5 mL). To this solution was added a solution of Eu(NO_3)₃·5H₂O (0.1079 g, 1 eq) in CH₃CN (4 mL). The two solutions were mixed and the solvents were allowed to evaporate over several days to afford the complex as a yellow solid (0.1791 g, 93 %). Mp 236–238 °C (decomposition). Found: C, 40.82; H, 3.68; N, 16.25%; $\text{C}_{26}\text{H}_{26}\text{O}_9\text{N}_9\text{Eu}$ requires C, 41.06; H, 3.45; N, 16.57%. $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 3103, 2936, 2869, 1643, 1598, 1575, 1463, 1447, 1430, 1373, 1298, 1273, 1246, 1183, 1166, 1149, 1112, 1066, 1027, 1014, 926, 844, 814, 780, 738, 721, 681, 653, 643, 630, 563. $\delta_{\text{H}}(400.1 \text{ MHz}; \text{CD}_3\text{CN})$ 2.68 (6H, s, 2 × Me), 2.91 (6H, s, 2 × Me), 3.04–3.07 (2H, m, CH_2), 3.11–3.14 (2H, m, CH_2), 3.44 (1H, d, J 7.8, ArH), 4.02 (1H, d, J 7.8, ArH), 4.91 (1H, br s, ArH), 6.29 (1H, t, J 7.8, ArH), 6.67 (1H, d, J 7.8, ArH), 7.01 (1H, d, J 7.1, ArH), 7.73 (1H, t, J 7.9, ArH), 8.45 (1H, d, J 7.1, ArH), 8.70 (1H, d, J 5.8, ArH), 9.29 (1H, t, J 7.8, ArH). $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CD}_3\text{CN})$ 29.4 (2 × Me), 32.1 (2 × Me), 32.8 (CH_2), 33.8 (CH_2), 36.2 (quat), 40.6 (quat), 93.6 (ArC), 94.4 (ArC), 95.9 (ArC), 98.8 (ArC), 100.4 (ArC), 110.7 (ArC), 116.9 (ArC), 131.8 (quat), 147.9 (ArC), 150.5 (ArC), 152.1 (ArC),

157.2 (quat), 174.6 (quat), 182.5 (quat), 191.2 (quat), 193.2 (quat), 193.3 (quat), 197.9 (quat). m/z (CI) 699.1210 (M^+); $[\text{C}_{26}\text{H}_{26}\text{O}_9\text{N}_8\text{Eu}]^+$ requires 699.1184. The complex (ca. 0.06 g) was dissolved in DCM (2 mL), toluene (5 mL) and CH₃CN (2 mL), and the resulting yellow solution was allowed to slowly evaporate affording crystals suitable for X-Ray analysis.

Ce(NO_3)₃ Complex of CyMe₄-hemi-BTBP **2**

The ligand **2** (0.1063 g, 0.2517 mmol) was dissolved in DCM (5 mL). To this solution was added a solution of Ce(NO_3)₃·6H₂O (0.1093 g, 1 eq) in CH₃CN (4 mL). The two solutions were mixed and the solvents were allowed to evaporate over several days to afford the complex as a yellow solid (0.1490 g, 79 %). Mp >300 °C (from DCM/MeCN). Found: C, 41.54; H, 3.41; N, 16.57%; $\text{C}_{26}\text{H}_{26}\text{O}_9\text{N}_9\text{Ce}$ requires C, 41.71; H, 3.50; N, 16.83%. $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 3093, 2968, 2933, 2871, 1632, 1597, 1575, 1529, 1460, 1445, 1428, 1372, 1290, 1245, 1182, 1149, 1112, 1065, 1026, 1009, 926, 844, 815, 781, 752, 733, 721, 681, 642, 541. $\delta_{\text{H}}(400.1 \text{ MHz}; \text{CD}_3\text{CN})$ 0.00 (6H, s, 2 × Me), 0.50 (6H, s, 2 × Me), 0.79–0.82 (2H, m, CH_2), 0.90–0.93 (2H, m, CH_2), 3.87 (1H, br s, ArH), 6.07 (1H, d, J 7.0, ArH), 6.40 (1H, d, J 8.2, ArH), 6.94 (1H, t, J 7.8, ArH), 6.98 (1H, d, J 8.0, ArH), 8.43 (1H, t, J 8.1, ArH), 8.50 (1H, d, J 7.8, ArH), 9.20 (1H, t, J 8.0, ArH), 9.51 (1H, d, J 8.0, ArH), 10.09 (1H, d, J 8.3, ArH). $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CD}_3\text{CN})$ 26.2 (2 × Me), 27.4 (2 × Me), 30.8 (CH_2), 31.4 (CH_2), 34.3 (quat), 36.8 (quat), 123.4 (ArC), 124.3 (ArC), 126.2 (ArC), 127.0 (ArC), 128.5 (ArC), 130.4 (ArC), 131.9 (ArC), 137.5 (ArC), 141.7 (ArC), 142.0 (ArC), 144.9 (quat), 146.8 (quat), 150.3 (quat), 154.8 (quat), 156.8 (quat), 157.7 (quat), 161.6 (quat), 164.7 (quat). The complex (ca. 0.045 g) was dissolved in DCM (2 mL), toluene (5 mL) and CH₃CN (2 mL), and the resulting yellow solution was allowed to slowly evaporate affording crystals suitable for X-Ray analysis.

UO₂(NO_3)₂ Complex of CyMe₄-hemi-BTBP **2**

The ligand **2** (0.015 g, 0.0355 mmol) was dissolved in DCM (1 mL). To this solution was added a solution of UO₂(NO_3)₂·6H₂O (0.0179 g, 0.0356 mmol, 1 eq) in MeOH (1 mL). To the resulting yellow solution was added CH₃CN (2 mL) and the solution was left to slowly evaporate affording crystals suitable for X-Ray crystallographic analysis.

CuBF₄ Complex of CyMe₄-hemi-BTBP **2**

The ligand **2** (0.0313 g, 0.07413 mmol) was dissolved in DCM (5 mL). To this solution was added a solution of [Cu(MeCN)₄]BF₄ (0.0233 g, 1 eq) in CH₃CN (4 mL). The two solutions were mixed and the solvents were allowed to evaporate over several days to afford the complex as a black solid (1.4:1 mixture of directional isomers, 0.0412 g, 97 %). Mp 265–268 °C (from DCM/MeCN). Found: C, 54.28; H, 4.85; N, 14.33; F, 12.97%; $\text{C}_{52}\text{H}_{52}\text{N}_{12}\text{B}_2\text{F}_8\text{Cu}_2$ requires C, 54.51; H, 4.57; N, 14.66; F, 13.27%. $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 3082, 2967, 2933, 2869, 1596, 1570, 1525, 1455, 1426, 1388, 1344, 1247, 1184, 1165, 1146, 1053, 816, 778, 750, 721, 680, 644, 625, 541. $\delta_{\text{H}}(400.1 \text{ MHz}; \text{CD}_3\text{CN})$ 1.16 (s, Me major and Me minor), 1.33 (Me minor), 1.39 (Me major), 1.44 (Me minor), 1.46 (Me major), 1.57 (Me major), 1.58 (Me minor), 1.81–1.93 (2 × CH_2 major and 2 × CH_2 minor), 7.30–7.36 (m, ArH major and minor), 7.89–7.92 (m, ArH major and minor), 7.94–8.10 (m, ArH major and minor), 8.14 (t, J 7.7,

ArH major), 8.28 (qu, *J* 4.1, ArH minor), 8.33 (dd, *J* 7.7 and 1.1, ArH major). δ_{C} (100.6 MHz; CD₃CN) 27.5 (Me major), 27.7 (Me minor), 28.3 (Me major), 28.5 (Me minor), 28.5 (Me minor), 28.6 (Me minor), 28.6 (Me major), 28.8 (Me major), 31.7 (CH₂ minor), 31.7 (CH₂ major), 32.5 (CH₂ minor), 32.6 (CH₂ major), 36.2 (quat), 36.3 (quat), 37.5 (quat), 37.5 (quat), 121.6 (ArC), 121.7 (ArC), 122.0 (ArC), 122.1 (ArC), 123.1 (ArC), 123.4 (ArC), 125.2 (ArC), 125.4 (ArC), 126.5 (ArC), 126.5 (ArC), 127.4 (ArC), 127.5 (ArC), 137.6 (ArC), 137.9 (ArC), 138.8 (ArC), 138.9 (ArC), 139.2 (ArC), 139.5 (ArC), 148.6 (ArC), 148.6 (ArC), 148.7 (quat), 149.0 (quat), 150.0 (quat), 150.1 (quat), 151.2 (quat), 151.4 (quat), 152.8 (quat), 153.2 (quat), 153.5 (quat), 153.8 (quat), 156.6 (quat), 156.8 (quat), 164.6 (quat), 164.8 (quat), 165.1 (quat), 165.7 (quat). *m/z* (CI) 485.1490 (M²⁺); [C₅₂H₅₂N₁₂Cu₂]²⁺ requires 485.1509.

AgBF₄ Complex of CyMe₄-hemi-BTBP 2

The ligand **2** (0.0349 g, 0.08265 mmol) was dissolved in DCM (5 mL). To this solution was added a solution of [Ag(MeCN)₄]BF₄ (0.0297 g, 1 eq) in CH₃CN (4 mL). The two solutions were mixed and the solvents were allowed to evaporate over several days to afford the complex as a light brown solid (0.0488 g, 95 %). Mp >300 °C (from DCM/MeCN). Found: C, 50.32; H, 4.17; N, 13.25; F, 11.96%; C₂₆H₂₆N₆BF₄Ag requires C, 50.60; H, 4.25; N, 13.61; F, 12.31%. ν_{max} (Nujol[®])/cm⁻¹ 3092, 2971, 2934, 2872, 1630, 1592, 1574, 1523, 1457, 1445, 1427, 1389, 1246, 1167, 1052, 1000, 922, 847, 816, 784, 747, 680, 639, 539. δ_{H} (400.1 MHz; CD₃CN) 1.21 (6H, s, 2 × Me), 1.50 (6H, s, 2 × Me), 1.84–1.87 (2H, m, CH₂), 1.89–1.92 (2H, m, CH₂), 7.28 (1H, ddd, *J* 7.9, 5.0 and 1.1, ArH), 7.83–7.85 (2H, m, 2 × ArH), 7.94 (1H, td, *J* 7.8 and 1.8, ArH), 8.09 (1H, d, *J* 4.2, ArH), 8.11 (1H, d, *J* 3.5, ArH), 8.15–8.22 (3H, m, 3 × ArH), 8.52 (1H, dd, *J* 7.2 and 1.5, ArH). δ_{C} (100.6 MHz; CD₃CN) 28.2 (2 × Me), 28.6 (2 × Me), 31.8 (CH₂), 32.4 (CH₂), 36.1 (quat), 37.3 (quat), 122.9 (ArC), 123.3 (ArC), 124.3 (ArC), 125.5 (ArC), 125.9 (ArC), 127.5 (ArC), 138.9 (ArC), 140.1 (ArC), 140.4 (ArC), 149.0 (quat), 150.2 (ArC), 150.3 (quat), 151.8 (quat), 154.6 (quat), 154.9 (quat), 156.1 (quat), 164.8 (quat), 166.8 (quat). *m/z* (CI) 529.1274 (M⁺); [C₂₆H₂₆N₆Ag]⁺ requires 529.1264.

X-ray Crystallography

For the structures of **2** and its uranyl complex, data were collected with Mo K α radiation at 100 K using the Oxford Diffraction X-Calibur CCD System (Oxford Diffraction XCalibur2 diffractometer equipped with an Oxford Cryosystems low temperature device). The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. For the structure of **2**, data analysis was carried out with the CrysAlis program.⁴¹ The structure was solved using direct methods with the Shelxs97 program.⁴² The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on *F*² using Shelxl97.⁴² For the uranyl structure, data were corrected for Lorenz and polarization factors and absorption corrections applied to all data. Using Olex2,⁴³ the structure was solved with the XS structure solution program using direct methods and refined with the XL refinement package using least squares

minimisation.⁴² For the Eu and Ce structures, data were collected with Cu K α radiation at 100.15 K using a Bruker APEX2 diffractometer using ϕ and ω scans.⁴⁴ The crystals were kept at 100.15 K during data collection. Bruker APEX2 was used to guide the diffractometer to collect a full set of diffraction images and perform unit cell determination. Data reductions were carried out by SAINT PLUS and multiscan absorption corrections were performed using SADABS.⁴⁵ The structures were solved using SUPERFLIP.⁴⁶ Using Olex2,⁴³ the structures were refined with the XL refinement package using least squares minimisation.⁴² Crystal Data have been deposited at the Cambridge Crystallographic Data Centre as CCDC 869233–869236. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Solvent Extraction Studies

The aqueous solutions were prepared by spiking nitric acid solutions (0.001–4 mol dm⁻³) with stock solutions of ²⁴¹Am and ¹⁵²Eu tracers (10 μ L) in nitric acid. The radiotracers ²⁴¹Am and ¹⁵²Eu were supplied by Isotopendienst M. Blaseg GmbH, Waldburg (Germany). Solutions of CyMe₄-hemi-BTBP **2** (0.01 mol dm⁻³) were prepared by dissolving **2** in *n*-octanol, with or without added 2-bromohexanoic acid. Each organic phase (500 μ L) was shaken separately with each of the aqueous phases (500 μ L) for one hour at 22 °C using an IKA Vibrax Orbital Shaker Model VXR (2,200 rpm). The contact time of one hour was sufficient to attain the distribution equilibrium. After phase separation by centrifugation, 200 μ L aliquots of each phase were withdrawn for radio analysis. Activity measurements of the γ -ray emitters ²⁴¹Am and ¹⁵²Eu were performed with a HPGe γ -ray spectrometer, EG-G Ortec. The γ -lines at 59.5 keV, and 121.8 keV were examined for ²⁴¹Am, and ¹⁵²Eu, respectively. The acidities of the initial and final aqueous solutions were determined by potentiometric titration against sodium hydroxide solution (0.1 mol dm⁻³) using a Metrohm 751 GPD Titrino device. The distribution ratio *D* was measured as the ratio between the radioactivity in the organic and the aqueous phase. Distribution ratios between 0.1 and 100 exhibit a maximum error of \pm 5 %. The error may be up to \pm 20 % for smaller and larger values.

Complexation Studies

The apparent stability constants β , equal to the molar ratio $[M_xL_y]^{x+y}/[M^{n+}]^x[L]^y$ (*M*^{*n*+} = cation, *L* = ligand), were determined by UV absorption spectrophotometry at 25.0 \pm 0.1 °C in methanol at a constant ionic strength provided by 10⁻² M Et₄NNO₃. The experimental procedure has been described in detail previously.²⁶ The spectral changes of 2 mL solutions of ligand **2** upon stepwise additions (50 μ L) of metal nitrate solution directly into the measurement cell were recorded from 250 to 370 nm with a Cary 3 (Varian) spectrophotometer. The ligand concentration was in the range 10⁻⁵–10⁻⁴ M. The data thus obtained were treated with the program Specfit.⁴⁷

NMR Titrations

Stock solutions (0.01 M) of the ligand **2** and of the metal salts La(NO₃)₃·6H₂O, Eu(NO₃)₃·5H₂O, Ce(NO₃)₃·6H₂O, Yb(NO₃)₃·6H₂O, Y(NO₃)₃·6H₂O, [Cu(MeCN)₄]BF₄ and

[Ag(MeCN)₄]BF₄ (Aldrich) were prepared in CD₃CN. A 0.5 mL aliquot of the ligand solution **2** was placed in an NMR tube and the ¹H NMR spectrum was recorded. The appropriate metal salt solution was added to the NMR tube in 50 µL aliquots (ie: 0.1 equivalents each time) using a calibrated Eppendorf 100 µL micropipette, the tube was inverted several times to ensure complete mixing and the ¹H NMR spectrum was recorded after each successive addition until the resonances of the free ligand had completely disappeared and/or until no further spectroscopic changes were observed. The relative ratios of the different species present were calculated from the relative integrals of a suitable one-proton resonance of **2**. These values were normalized such that, for a given one-proton resonance, the total integration for all species present equalled one. The species distribution at different metal:ligand ratios was calculated from these normalized relative ratios.

Acknowledgments

We thank the Nuclear Fission Safety Program of the European Union for support under the ACSEPT (FP7-CP-2007-211 267) contract. We also thank the EPSRC and the University of Reading for funds for the X-Calibur system. Use of the Chemical Analysis Facility at the University of Reading is gratefully acknowledged.

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- † Electronic Supplementary Information (ESI) available: [Procedures and characterization data for known compounds, Mercury plot of ligand **2** and its Eu, Ce and U complexes, NMR stack plots and species distribution curves, enlargements of mass peaks for La(III), Eu(III), Cu(I) and Ag(I) complexes of **2**]. See DOI: 10.1039/b000000x/
- ‡ Crystal data for **2**: C₂₆H₂₆N₆, *M* = 422.53, triclinic, spacegroup P-1, *Z* = 2, *a* = 8.5515(11), *b* = 8.5740(11), *c* = 16.214(2) Å, *α* = 81.677(11), *β* = 85.060(11), *γ* = 66.015(12)°, *T* = 100(2) K, *U* = 1074.2(2) Å³, *D*_c = 1.306 g cm⁻³, *μ* = 0.081 mm⁻¹, 5965 independent reflections, 2754 data (*I* > 2σ(*I*)), *R*₁ = 0.0539, *wR*₂ (all data) = 0.1063, CCDC 869235. Crystal data for [Eu(**2**)(NO₃)₃].2MeCN: C₃₀H₃₂EuN₉O₉, *M* = 842.63, monoclinic, space group P2₁/c, *Z* = 4, *a* = 12.8212(3), *b* = 14.9805(4)(8), *c* = 18.2654(5) Å, *β* = 102.155(2)°, *T* = 100.15 K, *U* = 3594.5(3) Å³, *D*_c = 1.632 g cm⁻³, *μ* = 13.688 mm⁻¹, 54007 independent reflections, 5561 data (*I* > 2σ(*I*)), *R*₁ = 0.0458, *wR*₂ (all data) = 0.1417, CCDC 869234. Crystal data for [Ce(**2**)(NO₃)₃].toluene: C₃₃H₃₄CeN₉O₉, *M* = 840.81, monoclinic, space group P2₁/n, *Z* = 4, *a* = 15.4789(8), *b* = 15.3507(8), *c* = 16.4216(8) Å, *β* = 112.897(3)°, *T* = 100.15 K, *U* = 3594.5(3) Å³, *D*_c = 1.554 g cm⁻³, *μ* = 13.052 mm⁻¹, 37812 independent reflections, 4468 data (*I* > 2σ(*I*)), *R*₁ = 0.0690, *wR*₂ (all data) = 0.1827, CCDC 869233. Crystal data for 2[UO₂(**2**)MeOH][UO₂(NO₃)₄]: U₃C₅₄H₆₀N₁₆O₂₀, *M* = 1966.7, triclinic, space group = P-1, *Z* = 1, *a* = 11.1976(8), *b* = 11.5470(8), *c* = 13.3767(10) Å, *α* = 113.4860(10), *β* = 99.1500(10), *γ* = 94.8080(19)°, *T* = 100(2) K, *U* = 1545.29(19) Å³, *D*_c = 2.113 g cm⁻³, *μ* = 7.929 mm⁻¹, 12300 independent reflections, 6198 data (*I* > 2σ(*I*)), *R*₁ = 0.0501, *wR*₂ (all data) = 0.0903, CCDC 869236.

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